



# A room temperature synthesizable and environmental friendly heterogeneous ZIF-67 catalyst for the solvent less and co-catalyst free synthesis of cyclic carbonates

Roshith Roshan Kuruppathparambil<sup>a</sup>, Tharun Jose<sup>a</sup>, Robin Babu<sup>a</sup>, Gyu-Young Hwang<sup>a</sup>, Amal Cherian Kathalikkattil<sup>a</sup>, Dong-Woo Kim<sup>b</sup>, Dae-Won Park<sup>a,\*</sup>

<sup>a</sup> School of Chemical and Biomolecular Engineering, Pusan National University, Busan 609-735, South Korea

<sup>b</sup> Korea Research Institute of Chemical Technology (KRICT), Division of Ulsan Research & Business Development, Research Center for Green Fine Chemicals, Yugok-dong, Jung-gu, Ulsan 681-802, South Korea

## ARTICLE INFO

### Article history:

Received 21 July 2015

Received in revised form 2 October 2015

Accepted 3 October 2015

Available online 9 October 2015

### Keywords:

CO<sub>2</sub> conversion

Cyclic carbonates

Heterogeneous ZIF-67 catalyst

Environmental friendly

Reusable

## ABSTRACT

Catalysts capable of materializing high performance without compromising the green credentials are a pre-requisite for the establishment of a sustainable process. Herein, ZIF-67, a cobalt based zeolitic imidazolate framework possessing acid-base bifunctionalities, is reported for its application in the artificial fixation of CO<sub>2</sub> via cyclic carbonate synthesis. The ZIF-67 is synthesizable in water at room temperature with inexpensive precursors in less than 3 h. The heterogeneous ZIF-67 was found catalytically efficient towards CO<sub>2</sub>-oxirane coupling under moderate reaction conditions with nearly complete selectivity towards five membered cyclic carbonates under solvent free and co-catalyst free conditions and it exhibited good reusability, outperforming the previously reported ZIF catalyst systems on efficiency and economic-environmental aspects. Crystal defects on the surface of the catalyst supposedly assumed to exert opportunistic catalytic roles in this liquid phase cycloaddition reaction and the plausible mechanism with multiple physico-chemical characterizations was proposed. In comparison with the previously reported heterogeneous catalysts synthesized by complicated multistep synthesis involving organic solvents and high temperature, the facile one-pot water mediated room temperature synthesis of ZIF-67 with acidic-basic dual active sites makes it more practical for high-performance heterogeneous catalysis ensuring green chemistry perspectives.

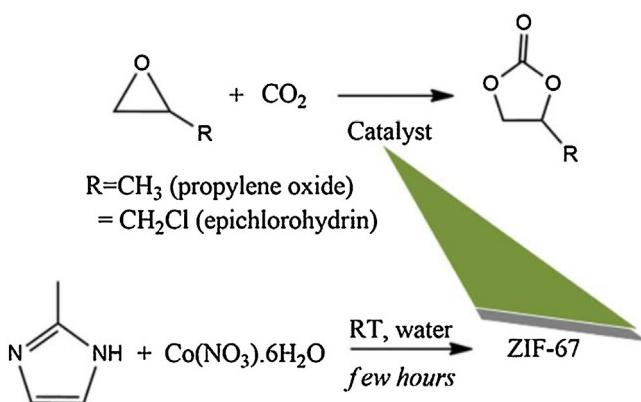
© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

The artificial fixation of CO<sub>2</sub> via the cycloaddition with epoxides has been widely acclaimed as a greener and the most commercial route to five membered cyclic carbonate syntheses, on aspects of global carbon management and resource utilization (Scheme 1). Five membered cyclic carbonates are industrially important compounds with a wide range of applications as polar aprotic solvents, electrolytes in Li ion batteries, monomers for polymer synthesis, degreasing agents, resins, cleaning, cosmetics and personal care products [1–5]. For the purpose, extensive number of catalysts belonging to both homo and hetero tags has been developed in the last few decades and the data collected was suggestive of a bi-functional catalyst with either a Lewis acid/base or Lewis

acid with a nucleophile to be the best catalytic motif to materialize CO<sub>2</sub>-epoxide cycloaddition [3]. Even though incompetent to homogeneous catalysts on a kinetic basis, much research was devoted to the development of heterogeneous catalysts, to aid easier separation and reusability. This was best exemplified by the immobilization of ionic liquids on supports such as silica [6–11], synthetic polymer resins [12–15] and biopolymers [16–20] which in general served appreciable catalysis in solvent free conditions however at temperatures of the order of 100 °C and 1 MPa CO<sub>2</sub> pressure or more. Notably, some researchers, especially North and co-workers [21–23] and Kleij and co-workers [24–27] were able to develop a number of metal complexes which along with quaternary ammonium halide co-catalysts procured promising catalysis even at room temperatures and atmospheric pressures. Whatever, an easily synthesizable robust single unit catalyst incorporating both acidic and basic sites which functions solvent and co-catalyst free still remain scarcely addressed.

\* Corresponding author. Fax: +82 515128563.  
E-mail address: [dwpark@pusan.ac.kr](mailto:dwpark@pusan.ac.kr) (D.-W. Park).



**Scheme 1.** Synthesis of cyclic carbonates from CO<sub>2</sub> and epoxides (above) and ZIF-67 from 2-methylimidazole (HmIm) and cobalt source.

Entered here, metal organic frameworks (MOFs), the renowned high surface area materials, enriching the library of advanced catalytic materials [28–33] by offering tunability over particle size, pore volumes, pore apertures, topology, ease of functionalization and seemingly innumerable versatility over acidic-basic properties with different metal centres and linkers; all of which were limited with the conventional CO<sub>2</sub> transformation catalysts such as metal oxides [34–36], ionic liquids [37–42], organic bases [43,44], metal complexes [21–27], phosphines [45] and supported ionic liquids [6–20]. Besides, MOFs possess an added advantage over these latter mentioned, such that, owing to its high CO<sub>2</sub> adsorption capability, MOF surfaces enhances the possibility of epoxide-CO<sub>2</sub> interaction multi fold times [46–55]. Unfortunately, the MOFs which served standalone catalysis (with no co-catalyst or solvent assistance) for CO<sub>2</sub>-epoxide cycloaddition represents only a small part of the whole family of MOFs.

In that case, Zeolitic imidazolate frameworks (ZIFs) stand out as the highlight materials, since they eventuated in catalysis even in the absence of any solvents or co-catalysts [56–59]. ZIFs form a subclass of MOFs which fundamentally consists of tetrahedral coordinated metal centres (typically Zn and Co) and imidazole derivatives [60,61].

Since the first report of ZIF-8 catalysed epichlorohydrin-CO<sub>2</sub> cycloaddition by Miralda et al. [56], a few other ZIFs such as ZIF-90, F-ZIF-90 [57] and ZIF-68 [59], were investigated for the same application in the recent years and to mention, all of them consisting of Zn as their Lewis acidic centre. Here in this work, we are investigating, a Co based ZIF (ZIF-67) for its catalytic potential for CO<sub>2</sub>-epoxide cycloaddition (**Scheme 1**). But more than merely reporting this application of Co based ZIF catalyst for CO<sub>2</sub>-epoxide cycloaddition, our emphasis relied critically on analysing the fulfilment of certain green chemistry principles, such as the ease-inexpensiveness and environmental friendliness of the catalyst synthesis, air, water, thermal and chemical stability, reusability with least activation and the non-leaching properties of the synthesized catalyst ZIF-67; which we have carried out by comparing this work to the reported ZIFs so far in this area of CO<sub>2</sub> transformation. While turnover frequency (TOF) adorned the standard measure to evaluate the efficiency of a catalyst, the above mentioned green criteria are often overlooked. ZIF-90 and ZIF-68 used 2-carboxaldehyde imidazole (ICA) and 2-nitroimidazole (nlm) as linkers, respectively, which were both nearly 300 and 1500 times expensive than the ZIF-67 linker (2-methylimidazole, HmIm). This may limit the application of the former on a larger scale. While ZIF-8 uses the same linker as ZIF-67, the catalysis with the former which inhabits Zn as the Lewis acidic centre was reported to compromise its selectivity towards the desired cyclic carbonate at elevated temperatures by either inducing polymerizations [57] or

diol/dimer formations with the epoxide substrates [56]. The artificial fixation of CO<sub>2</sub> via cyclic carbonate synthesis adorns the tag of being green owing to its 100% atom economic nature, and hence it is imperative to bring forth high selectivity [62]. In the following sections we have attempted to illustrate the handiness and judiciousness of choosing ZIF-67 as an aqueous and room temperature synthesizable catalyst for artificial CO<sub>2</sub> fixation owing to its high selectivity and economic-environmental friendly aspects.

## 2. Experimental

2-Methylimidazole (HmIm) (99%) and all the epoxides were bought from Sigma-Aldrich, Korea and the metal salts (>99%) were bought from TCI chemicals. CO<sub>2</sub> (99%) and double distilled water was used for synthesis and washing purposes.

### 2.1. Synthetic procedure

HmIm was dissolved in double distilled water and followed the addition of an aqueous Co(NO<sub>3</sub>)<sub>6</sub>H<sub>2</sub>O solution with stirring. Purple colored product was formed instantaneously at room temperature. Stirring kept for a few hours (2–3) and then centrifuged at 9000 rpm for three times. Washed with water for few more times and then kept for drying in the oven at 80 °C overnight under vacuum.

### 2.2. CO<sub>2</sub>-epoxide cycloaddition

All the reactions were carried out in a 25 mL stainless-steel batch reactor with a magnetic stirrer at 600 rpm. In a typical batch reaction process, a pre-decided amount of the catalyst was charged into the reactor containing 25 mmol of the epoxide. The reaction was carried out under various temperatures and pressures of carbon dioxide with different reaction times. After the completion of the reaction, the reactor was cooled to room temperature (zero degree in case of propylene oxide) and the products were identified by a gas chromatograph (Agilent HP 6890 A) equipped with a capillary column (HP-5) using a flame ionized detector. The product yield was determined by using toluene as internal standard.

### 2.3. Characterizations

The synthesized ZIF-67 was characterized according to the previous reports [61,63–69] using a range of analysis methods. The elemental analysis (EA) was carried out using a Vario ELIII system. Two milligram of the sample was subjected to analysis at 1100 °C, and sulfanilic acid was used as the standard. Fourier transform infrared (FT-IR) spectra were obtained on an AVATAR 370 Thermo Nicolet spectrophotometer with a resolution of 4 cm. Thermogravimetric analysis (TGA) was conducted with an AutoTGA 2950 apparatus with a heating rate of 10 °C/min from 40 °C to 600 °C in nitrogen under a flow of 100 mL/min. The X-ray diffractions (XRD) were recorded as powders in a Rigaku Ultima IV diffractometer using the Cu K $\alpha$  radiation (40 kV, 40 mA) with step size  $\Delta 2\theta = 0.02^\circ$ , time per step = 4 s. The surface area was determined to be 1374 m<sup>2</sup>/g (BET area) by N<sub>2</sub> adsorption at 77 K using a Micromeritics ASAP 2020 instrument. The surface morphology was observed using a S-4200 field emission scanning electron microscope (FE-SEM, Hitachi-3500N). The metal contents of the catalysts were obtained from ICP-OES analysis using ULTIMA2CHR (1.5 kW, 40.68 MHz, 130–800 mm) with mono chromato HDD and a poly chromato PMT detector.

**Table 1**  
Catalytic tests.

Catalyst	Conversion <sup>b</sup> (%)	Selectivity <sup>b</sup> (%)
1 HmIm (−120)	2	—
2 HmIm (100)	15	94
3 Co(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O (100)	7	95
4 HmIm + Co(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O (100)	44	95
5 ZIF-67 (100)	76	99
6 HmIm (120)	61	89
7 Co(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O (120)	11	61
8 HmIm + Co(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O (120)	78	70
9 ZIF-67 (120)	97	98
10 ZIF-67 (120) reuse 1	96	98
11 <sup>a</sup> ZIF-67 (120)+water	97	98

Reaction conditions: mentioned above in brackets is the temperature of reaction. Epichlorohydrin (ECH) 25 mmol, catalyst = 0.5 mol%, ZIF-67 = 30 mg [0.13 mmol Co = 0.5 mol%, from ICP-OES], 7 bar CO<sub>2</sub>, 6 h

<sup>a</sup> ECH (25 mmol), ZIF-67 (30 mg), water (0.01 mL), 4 h, 7 bar.

<sup>b</sup> Obtained from the GC (specifications are mentioned in the experimental section).

**Table 2**  
Catalytic activity comparison of ZIFs.

Catalyst	Conversion(%)	Selectivity(%)	Refs.
1 <sup>a</sup> ZIF-8	98.2	33.4	[56]
2 <sup>a</sup> F-ZIF-8	100	49.1	[56]
3 <sup>a</sup> ZIF-67	63.5	>99	This work
4 <sup>b</sup> ZIF-68	50	100	[59]
5 <sup>b</sup> ZIF-67	87	>99	This work
6 <sup>c</sup> ZIF-90	64.8	61.8	[57]
7 <sup>c</sup> F-ZIF-90	76.9	94.6	[57]
8 <sup>c</sup> ZIF-67	69	>99	This work

Conditions.

<sup>a</sup> ECH, 100 °C, 4 h, 7 bar, 0.7 mol% catalyst.

<sup>b</sup> SO (styrene oxide), 120 °C, 6 h, 10 bar, ZIF-68 (100 mg), ZIF-67 (50 mg).

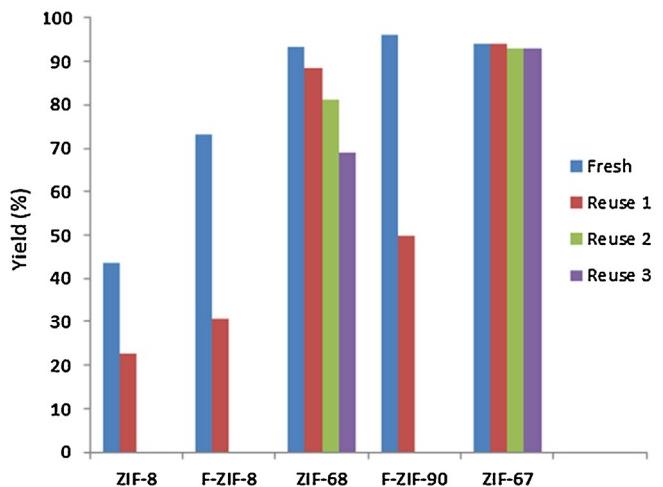
<sup>c</sup> AGE (allylglycidylether), 120 °C, 6 h, 12 bar, 0.18 mol% catalyst.

### 3. Results and discussion

#### 3.1. Catalytic performance

Epichlorohydrin (ECH) was chosen as the model substrate to evaluate the catalysing ability of ZIF-67. Requisite amount of the as-synthesized catalyst was charged and the parameters were varied accordingly. As is widely known, even though the CO<sub>2</sub> cycloaddition in general is a highly exothermic reaction, no product formation was observed in the absence of a catalyst (entry 1, Table 1). The precursors of ZIF-67, viz, Co(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O and HmIm both were examined for their individual catalytic potentials in entry 2, 3, 6 and 7 as well as the combination of both (entry 4, 8). Out of its basic character, HmIm yielded a conversion of 15% and 61% at 100 °C and 120 °C, respectively (entry 2, 6). Organic bases were previously been reported to catalyse this reaction to different extents under varied conditions. The combination of Co(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O and HmIm (entry 4, 8) afforded improved results, however, only inferior to ZIF-67 (entry 5, 9). Under the employed reaction conditions, ZIF-67 manifested >97% conversion of ECH with an excellent selectivity of >99% (entry 9) to its corresponding cyclic carbonate, which is epichlorohydrin carbonate. Even though the precursor mixtures were active, unlike ZIF-67 they became homogeneous with the epoxide-cyclic carbonate-CO<sub>2</sub> reaction matrix and were unable to separate for further use. However, ZIF-67 framework exhibited excellent chemical stability to the reaction mixture even at a temperature of 120 °C, wherein mere centrifugation followed with ethanol wash regenerated the catalyst with apparently no or negligible mass loss (reusability data is given later as Fig. 1).

Table 2 gives a summarized data of the activity shown by various ZIFs. To make a direct comparison with its Zn containing analogue



**Fig. 1.** Yields of cyclic carbonate after reuse for ZIFs, ZIF-8 and F-ZIF-8 (ECH, 80 °C) [56], ZIF-68 [59] (SO, 120 °C), ZIF-90 [57] and ZIF-67 (this work) (AGE, 120 °C).

(ZIF-8), the catalysis was carried out at the same conditions as of Miralda et al. [56]. The results were such that, while ZIF-8 was reported to give 98.2% conversion of ECH with only 33.4% selectivity to the desired product (18 mmol ECH, 0.13 mmol Zn, 100 °C, 4 h, 7 bar CO<sub>2</sub>), the ZIF-67 consisting of Co, produced only 63.5% ECH conversion, however without compromising the selectivity to epichlorohydrin carbonate (>99%) and shown excellent reusability (Fig. 1). While ZIF-8 was irrevocably lost after the reaction, the Co based ZIF-67 was totally recyclable. Even at milder reaction conditions (80 °C), the selectivity with ZIF-8 was only 52% to EPC (43.7% EPH yield, Fig. 1) which got reduced to 22.1% yield upon first reuse. This observation shall be surmised as follows; the Zn being more reactive towards epoxide (as is evident from the 98.2% ECH conversion, entry 1, Table 2) engages in stronger interactions with the substrate which may have eventually weakened the framework spine of Zn–N bonds (Zn-imidazole), and the structural collapse occurred inevitably. This may have led to the uneven distribution of intermolecular forces which resulted in its declined selectivity. At the same time, the Co framework of ZIF-67 was only moderately active towards the epoxide molecule as reflected by its lower ECH conversion rate (compared to ZIF-8, entry 3, Table 2), but maintained the necessary motive of 100% atom economy by possessing more than 99% selectivity to the desired product, thereby eliminating the need for any energy intensive time consuming separating process. According to TPD analysis, the Zn-ZIF-8 possesses strong Lewis acid sites while the Co-ZIF-67 accommodates only moderately strong Lewis acidic properties, which may rationale the above observation [70]. It has been generally known that, selectivity is of greater importance than activity since a highly selective catalyst/process eliminates the need for usual separation procedures which often involve the use of considerable amounts of organic solvents and energy [71,72]. At this point it is noteworthy to consider entry 5 of Table 1, that even at higher temperature (120 °C), the selectivity to epichlorohydrin carbonate (ECC) was not compromised with ZIF-67 demonstrating the balance of framework stability and activity of this material.

As mentioned earlier in the introductory section, ZIF-68 and ZIF-90 were also reported for their catalysis in the CO<sub>2</sub>-epoxide cycloaddition. A direct comparison of the catalytic performance of ZIF-68 with ZIF-67 was tedious since the catalyst amount in mol% was not mentioned [59]. However, ZIF-67 (entry 5, Table 2) showed 87% conversion of SO in 6 h and 120 °C whereas the SO conversion was nearly 50% with ZIF-68 in 6 h, 120 °C [59]. Entries 6–8 clearly shows that the performance of ZIF-90 and F-ZIF-90 (F stands for functionalization done using quaternized groups) in CO<sub>2</sub>-AGE

(ZIF-8 and 67)	(ZIF-90)	(ZIF-68)
Hmim	ICA	nIm      bIm
37 \$ / 100 g	118 \$ / 1 g	574 \$ / 1 g      78 \$ / 100 g
Methanol/water RT, few hours [56]	DMF, 100°C, 18 h [58]	DMF, 100°C, 72 h [59]

**Scheme 2.** Synthesis particulars of various ZIFs employed for CO<sub>2</sub>-epoxide cycloaddition [the cost of the different imidazoles are as per the Sigma-Aldrich ([www.sigmadlrich.com](http://www.sigmadlrich.com))].

cycloaddition was also inferior to that achieved with ZIF-67. While the selectivity of ZIF-90 and F-ZIF-90 rested at 62 and 95% of cyclic carbonate respectively, ZIF-67 once again exhibited complete selectivity which is a notable result. Hence it is clear that, on the scales of activity profiles, ZIF-67 stays along or a step ahead of the reported ZIFs so far, by maintaining its excellent selectivity to the corresponding cyclic carbonate without compromising the conversion rate. Should this way of carbon dioxide capture and utilization finds new dimensions on a larger scale, 100% atom economy is a necessary criteria and thus the catalysts manifesting high selectivity even at higher temperatures are highly desirable [22,62].

While it is clear that, the CO<sub>2</sub>-epoxide cycloaddition would not proceed under catalyst free conditions, the economic feasibility and environmental friendliness of the catalyst synthesis is a deciding factor in ensuring sustainability. **Scheme 2** gives an estimated comparison of the aforementioned criteria. While ZIF-8 and ZIF-67 made use of 2-methylimidazole (HmIm) as the linker, a mixture of benzimidazole (bIm) and 2-nitroimidazole (nIm) forms the organic linker for ZIF-68 and 2-carboxaldehyde imidazole (ICA) for ZIF-90. nIm is a highly expensive linker (nearly 1500 times expensive) compared to HmIm. ICA is also comparatively expensive by about 300 times to HmIm. Also, while ZIF-67 is synthesizable at room temperature in water media under a few minutes reaction time, ZIF-68 and ZIF-90 demanded autoclave conditions and included high boiling organic solvents. It is to be noted that, with the continuous update occurring in the ZIF related research, an increasing number of ZIFs are nowadays synthesizable under aqueous conditions at the expense of some inorganic bases. But the most remarkable thing to be exalted here is that, the linker for ZIF-67 is readily available and cheap. ZIFs are more likely to be used for any cost sensitive purpose if they can be synthesized at low cost using energy efficient syntheses. And, since water is used as the reaction media, and also the ZIF-67 made as such did not require any further activation steps such as solvent exchange or sonication prior to the catalytic purposes, the environmental aspects of the ZIF-67 mediated cyclic carbonate synthesis shall have thought to be preserved to a significant extent (not to mention the high selectivity achieved by ZIF-67 throughout the catalysis).

### 3.2. Reusability study

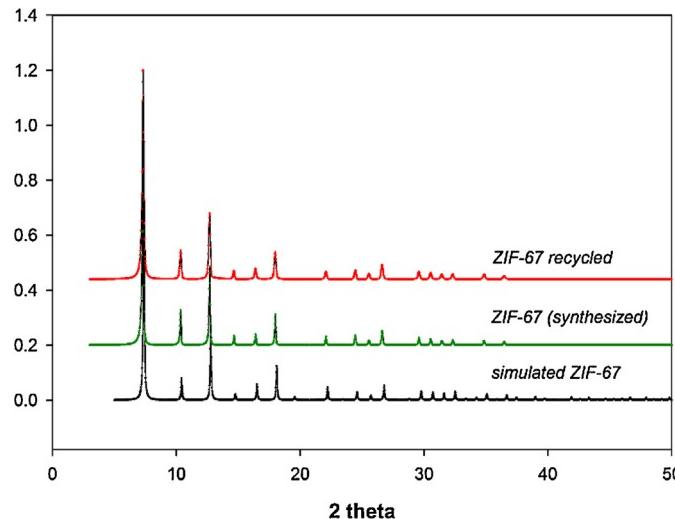
Another important benchmark to be considered in heterogeneous catalysis is the reusability (**Fig. 1**). ZIF-67 has accomplished excellent reusability in terms of epoxide conversion and selectivity to the desired cyclic carbonate without any observable loss. While the yields of the corresponding cyclic carbonates upon the first reuse of the catalyst declined to nearly half or even lower with ZIF-8, F-ZIF-8 and F-ZIF-90, the reusability performance with ZIF-68

**Table 3**  
ICP-OES and elemental analysis data of ZIF-67 and recycled ZIF-67.

	Co%	C%	H%	N%
ZIF-67 (fresh)	25.7	42.0	4.3	24.6
ZIF-67 (1st recycle) <sup>a</sup>	24.9	42.5	5.1	25.2

wt% is mentioned.

<sup>a</sup> AGE 25 mmol, 120 °C, 10 bar, 6 h.

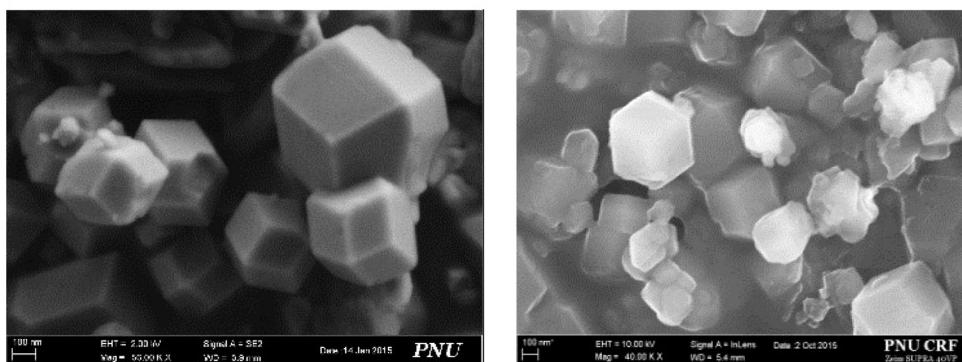


**Fig. 2.** XRD of ZIF-67 simulated, synthesized and first recycled.

was appreciable [56–59]. The yield of styrene carbonate (from the cycloaddition of CO<sub>2</sub> and styrene oxide) with ZIF-68 followed the order of 93.3–88.3% upon first recycle and ended up with a figure of 66.4% after the third recycle [59]. Here again, ZIF-67 excelled in its properties, such that, even after recycling for three times, the yield of the cyclic carbonate did not diminish to any significant extent. In recent reports, Schejn et al. and Yang et al. have also illustrated the reusable nature of ZIF-67 catalysts in organic reactions [64,70].

The ZIF-67 catalyst from the reaction mixture was separated via centrifugation followed by washing with ethanol and successively dried at 80 °C for 4 h and used again. The Co content of the fresh ZIF-67 was determined to be 25.7wt% by ICP-OES which was verified with the literature data [56]. ICP-OES of the first recycled ZIF-67 (entry 2, **Table 3**) showed that the Co content was 24.9% which was not much lower than the value determined for the fresh ZIF-67 (25.7%). Also, the filtrate of the reaction matrix after carrying out the reaction of ECH-CO<sub>2</sub> for 6 h with 7 bar pressure at 120 °C was analysed and found that only less than 1wt% Co was found in the filtrate which indicated that the leaching percentage of ZIF-67 was remarkably lower compared to that of the ZIF-8 (nearly 90% Zn was leached from ZIF-8 at 80 °C in 4 h with ECH-CO<sub>2</sub> reaction [56]), which rationalized the higher reusability performance of ZIF-67 compared to ZIF-8. We believe that, the determination of leached amount of the metal species (if any) in the reaction medium is of great importance since it is indispensable to understand the true origin of the catalytic activity.

The XRD of the recycled catalyst remained essentially same as that of the fresh ZIF-67 (**Fig. 2**), which gave a direct evidence of structural stability possessed by ZIF-67 under the conditions employed for the cyclic carbonate synthesis [61,63,64]. **Fig. 3** displays the FE-SEM images of the fresh ZIF-67 and the used one. The synthesized ZIF-67 particles exhibited truncated rhombic dodecahedral shape with size range of 200–500 nm, while after the first use several perturbations has been found on the crystal morphology. The TGA and FT-IR comparison for the fresh ZIF-67 and the recycled ZIF-67 are given in the ESI, as Fig. S1 and S2, respectively. ZIF-67



**Fig. 3.** FE-SEM images of the fresh ZIF-67 (left) and the first recycled ZIF-67 (right).

possessed a high thermal stability of nearly 550 °C, and the recycled catalyst displayed an earlier onset of weight loss at 200 °C (most likely attributable to the removal of the molecules occluded or surface bound to the ZIF-67 during the course of reaction) while the framework degradation occurred around 500 °C which was characteristic to the fresh ZIF-67. The similarity in the FT-IR spectra of fresh and recycled catalyst illustrated that the chemical environment of ZIF-67 was well preserved even after subjected to the reaction conditions of cycloaddition employed to obtain the maximum activity (120, 7 bar, 6 h).

### 3.3. Reaction parameter optimization

To optimize the process, reaction parameter study was carried out (Fig. 4). The temperature scans (Fig. 4a) clearly indicated the crucial role of thermal activation such that, with nearly zero conversion at 40 °C, the catalytic activity linearly increased till 100 °C and reached the maximum at 120 °C with 0.5 mol% of catalyst and 7 bar CO<sub>2</sub> pressure in 6 h. Further increase in temperature was conducted and even at 140 °C, 96% selectivity to epichlorohydrin carbonate was retained with the ZIF-67 catalyst. At this point, it seems appropriate to mention that the key objective in catalysis research is improving selectivity [71].

Fig. 4b indicates that, the kinetics of the reaction followed the concentration of CO<sub>2</sub> in a specific way. With not more than 15% conversions till 4 bar, the ECH conversion shoot up to nearly 97% when the pressure reached 7 bar and stayed as such even at pressures of 20 bar. However, further increase in CO<sub>2</sub> pressure (above 30 bar) was met with the consequence of a reduction in epichlorohydrin conversion probably since too high a pressure may retard the interaction of ZIF-67 with the epichlorohydrin, also known as the dilution effect as reported in previous works [8,10,54]. Since, the ZIF mediated CO<sub>2</sub>-epoxide coupling essentially involves a tri-phasic system, the excess amounts of the dissolved CO<sub>2</sub> may hinders the interaction of epoxide molecules with the active centres on the outer surface of the catalyst which may be the reason for the decrease in conversion rate with higher pressures. However, this activity shown by ZIF-67 even at 7 bar pressure under this solvent free and co-catalyst free conditions clearly reflects the significance of employing catalysts with high CO<sub>2</sub> adsorption for CO<sub>2</sub> transformations as well.

Fig. 4c and d, respectively shows the influence of time and catalytic amounts in the ZIF-67 mediated catalysis of CO<sub>2</sub>-ECH cycloaddition. It was found that 6 h reaction time and 0.5 mol% catalyst was ample enough to attain the maximum conversion of ECH at 120 °C with 7 bar pressure.

To ascertain the versatility of the catalyst, various epoxides were reacted with CO<sub>2</sub> under the conditions optimized. As shown in Table 4, while the terminal aliphatic epoxides were converted

**Table 4**  
Catalytic activity of ZIF-67 for various epoxides.

	Epoxide	Conversion(%)	Selectivity(%)
1	Allylglycidylether	94	98
2	Epichlorohydrin	97	99
3	Propylene oxide	98	99
4	Styrene oxide	73	97
5	Cyclohexene oxide	8	98

Reaction conditions: epoxide 25 mmol, ZIF-67 (30 mg), 120 °C, 10 bar, 6 h.

nearly to its maximum with selectivity to its corresponding cyclic carbonate no lesser than 98%, the internal epoxide, cyclohexene oxide remained hard to crack under the employed reaction conditions. This has been the scenario for most of the catalysts reported in CO<sub>2</sub>-epoxide cycloaddition and is widely been ascribed to the steric hindrance caused by the cyclohexene ring.

### 3.4. Reaction mechanism

ZIFs are “saturated” frameworks in the sense that, ideally they are devoid of any low-coordinated structural metal atoms, and the linkers are not functionalized (other than to the metal centre) and hence, a priori, ZIFs should not show catalytic properties [73]. However, a number of ZIFs have already been reported for several catalytic transformations [74] which includes, transesterification, Knoevenagel reaction, Friedel-Crafts acylation, monoglyceride synthesis, synthesis of carbonates, oxidation and epoxidation, and hydrogen production. The mechanisms of most of these are credited to the “opportunistic catalysis”, as it was called by Hupp and co-workers [75]. A detailed study including analytical and DFT cluster calculations reported by Chizallet et al. [73], in the case of ZIF-8 mediated transesterification of vegetable oil shed more insights into the above mentioned mode of catalysis. As per their results, acidic-basic sites located at the external surface of the ZIF catalyst or at the defects are responsible for the catalysis. If only, the extrapolation of the ZIF-8 based catalytic routes to ZIF-67 is amenable, then a large variety of species shall co-exist on the ZIF-67 external surface too. These species may include OH and NH groups, hydrogenocarbonates, low-coordinated Co atoms, and free N-moieties belonging to the linkers. The proportion of low coordinated Co atoms such as Co<sub>III</sub> nodes and Co<sub>II</sub> nodes depends on the number of linkers lost around the exposed Co centre. According to the TPD data, ZIF-67 possesses moderately strong acid-base sites which shall be surmised to the presence of Co<sub>II</sub>-Co<sub>III</sub> species and N<sup>−</sup> moieties. The presence of small amounts of atmospheric moisture may lead to the formation of NH, −OH and hydrogenocarbonate species on the ZIF surface as depicted in the Scheme 3. These groups, especially NH and OH have accelerating effects in the CO<sub>2</sub>-epoxide catalysis as have experimentally proved and computationally validated by

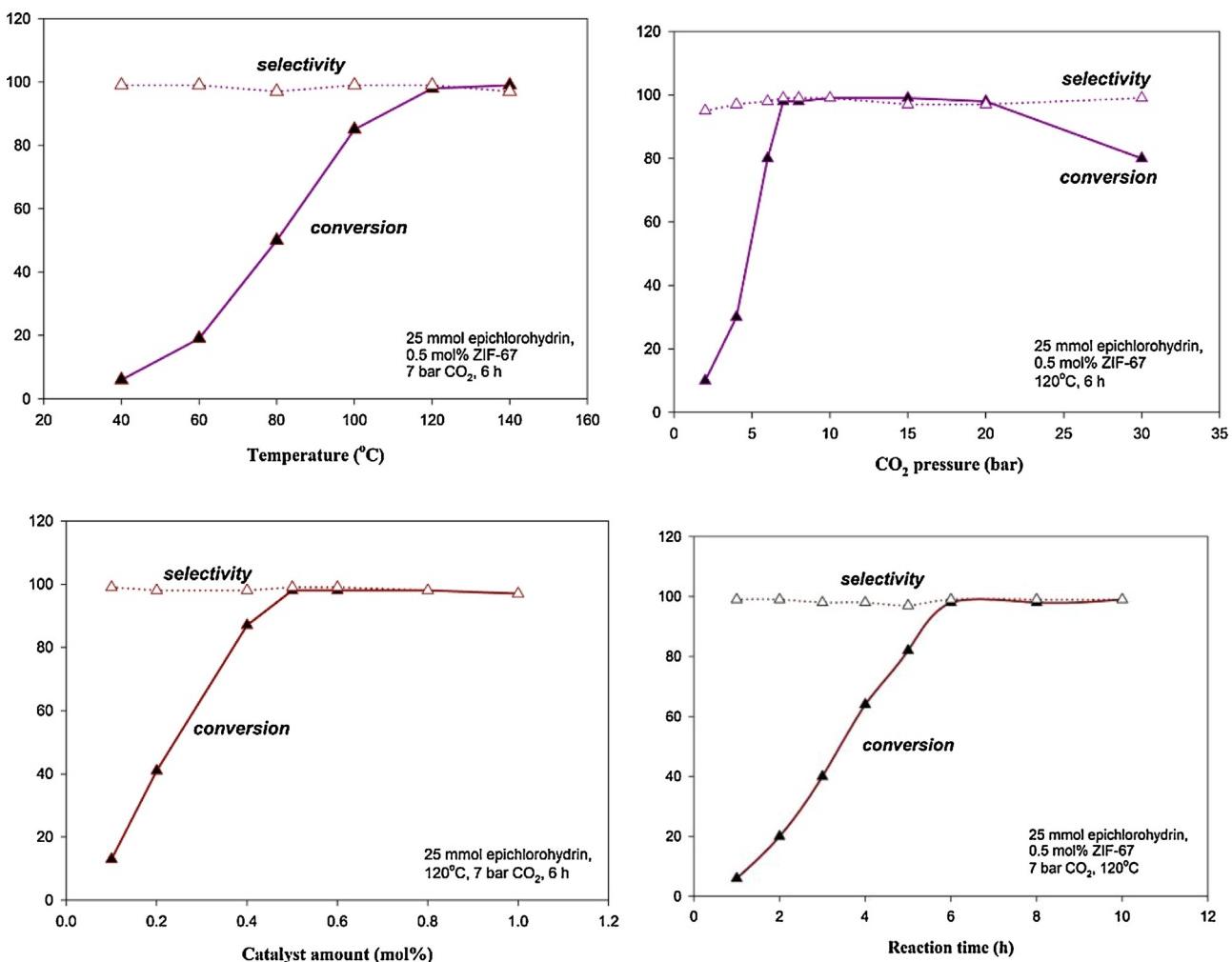
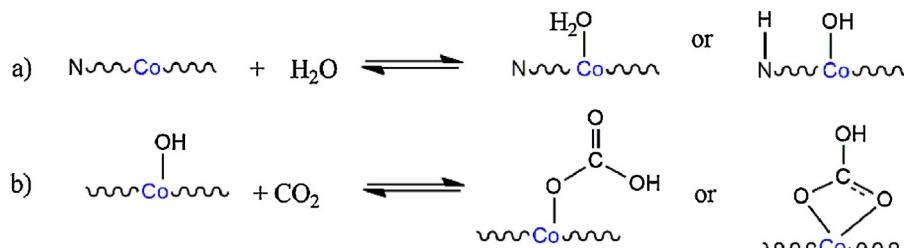


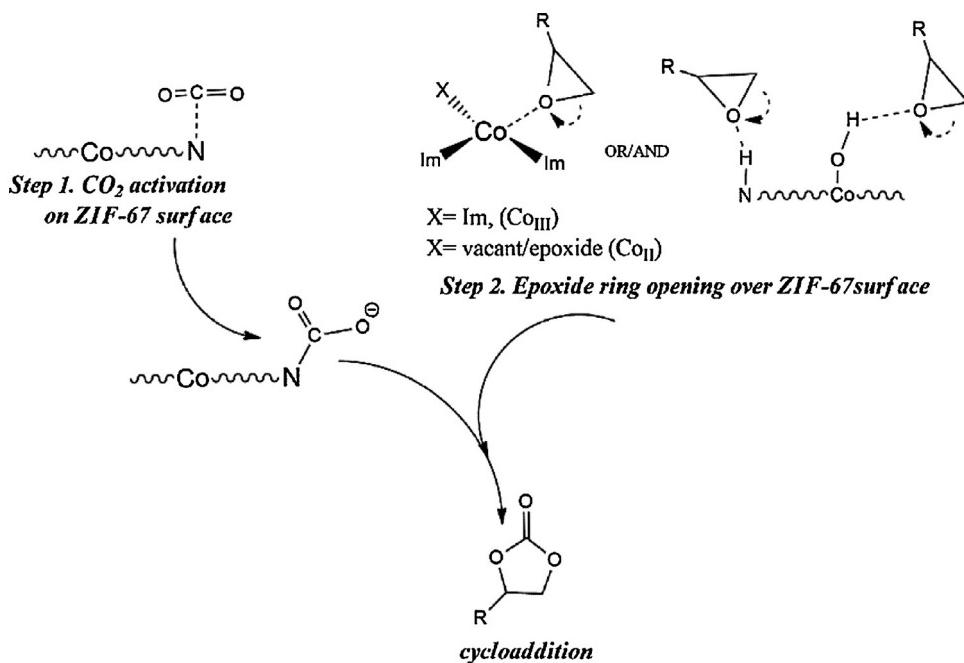
Fig. 4. Reaction parameter study.

Scheme 3. Expected species on the external chemical surface of ZIF-67 in the presence of water and CO<sub>2</sub>.

numerous reports [6,10,16,17,76]. Also, the observation that, the catalysis rate was accelerated with small amounts of water added to the reaction mixture (entry 11, Table 1) supplements this rationale. Recently we reported the DFT study results on the role of ZIF-90 for propylene oxide-CO<sub>2</sub> reaction [77]. Hence the catalytic activity shown by ZIF-67 in the case of epoxide-CO<sub>2</sub> cycloaddition yielding cyclic carbonates shall have involved the acid-base sites on the external surface of the catalyst (Co<sub>II</sub>, Co<sub>III</sub> and N<sup>-</sup> moiety) as well as these opportunistic hydrogen bonding groups formed during the course of the reaction. Scheme 4 depicts a plausible pathway of the sequence of events occurred during the ZIF-67 mediated cyclic carbonate synthesis. The coordinatively unsaturated Co centres (Co<sub>II</sub>/Co<sub>III</sub>) or/and the OH/NH groups on the external surface of ZIF-67 activates the oxygen atom of the epoxide, whereby the βC-O bond weakens and ring opening occurs, leading to the formation of

a partial positive charge on the β carbon atom of the epoxide. The basic moieties (N<sup>-</sup> group) at the extremity of the mono coordinated imidazolate ligand initiate a nucleophilic attack on the C atom of CO<sub>2</sub>, due to which, one of the oxygen atom of CO<sub>2</sub> acquires a partial negative charge. Considering the results of our recent study on ZIF-90 mechanism using DFT, the CO<sub>2</sub> activation may occur in the first place [77]. Now that, both the ring opened epoxide and the activated CO<sub>2</sub> molecule is ready, materializes the cycloaddition to form the final product, cyclic carbonate, and the catalyst is set to begin the new cycle.

While the catalytic space of applications of MOFs is increasing with the available number of examples and catalytic reactions, the main agenda is to encapsulate certain active species inside the pores of the MOFs or to implement post-functionalization techniques to improve the activity/selectivity. But those studies meant



**Scheme 4.** Plausible reaction mechanism of  $\text{CO}_2$ -epoxide cycloaddition catalyzed on the ZIF-67 surface.

at exploiting the catalysis performed by the defects on the crystal surface of the MOFs are rather rare. In case of the industrial catalysts such as the metal oxides, it is of common knowledge that, Lewis acid (coordinatively unsaturated cations) and basic sites (oxide anions) are normally associated with the surface and are of paramount importance in devising certain catalytic routes. We hope that, this ZIF mediated  $\text{CO}_2$  fixation is poised with such great possibility of utilizing the defects on the MOF surface. Since, the thermodynamic considerations imply that all the crystals must contain a number of defects at non-zero temperature, synthesizing ZIFs or MOFs with defects capable of commencing “opportunistic catalysis” would not be a Herculean task.

#### 4. Conclusions

ZIF-67 is a Co based imidazolate metal organic framework, synthesizable in water media at room temperature in few hours' time. ZIF-67 catalysed the cycloaddition of  $\text{CO}_2$  and epoxides forming cyclic carbonates in high yields with nearly 100% atom economy under solvent free and co-catalyst free conditions. The economic and environmental benign nature of this catalyst has been found to excel over the other ZIFs reported for this reaction. It shall be concluded that, while the Zn containing ZIF-8 is more reactive towards epoxide- $\text{CO}_2$  reaction, the Co containing ZIF-67 renders better selectivity. ZIF-67 was totally reusable without any severe activation steps and the ICP-OES analysis of the filtrate revealed that, only a very small percentage (<1%) of leaching occurs to the catalyst under the conditions rendering the highest conversion rate of the epoxide. XRD and TGA analysis of the recycled catalysts assured that, the framework of ZIF-67 is quite stable even after reuses. The structural defects on the external surface of the catalyst affords a specific acid-base property and is thought to rationale the catalytic activity shown by ZIF-67, and in general by all ZIF materials. We believe that, ZIFs, particularly those which are synthesizable from inexpensive linkers under greener reaction conditions and those which displays high catalytic efficiency for artificial  $\text{CO}_2$  fixation, under solvent free and co-catalyst free conditions holds bright promise towards establishing sustainable green processes.

#### Acknowledgements

This study was supported by the National Research Foundation of Korea through global frontier project (GF-HIM 2015M3A6B1065264) and Basic Research Programme (2014-2055412). Roshith is thankful to the financial support by the 2015 PNU Post-Doc program.

#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2015.10.005>.

#### References

- [1] M. Mikkelsen, M. Jorgensen, F.C. Krebs, *Energy Environ. Sci.* 3 (2010) 43–81.
- [2] T. Sakakura, J. Choi, H. Yasuda, *Chem. Rev.* 107 (2007) 2365–2387.
- [3] M. North, R. Pasquale, C. Young, *Green Chem.* 12 (2010) 1514–1539.
- [4] N. Kielland, C.J. Whiteoak, A.W. Kleij, *Adv. Synth. Catal.* 355 (2013) 2115–2138.
- [5] J.W. Comerford, Ian D.V. Ingram, M. North, X. Wu, *Green Chem.* 17 (2015) 1966–1987.
- [6] T. Takahashi, T. Watahiki, S. Kitazume, H. Yasuda, T. Sakakura, *Chem. Commun.* 15 (2006) 1664–1666.
- [7] J.Q. Wang, X.D. Yue, F. Cai, L.N. He, *Catal. Commun.* 8 (2007) 167–172.
- [8] L. Han, S.W. Park, D.W. Park, *Energy Environ. Sci.* 2 (2009) 1286–1292.
- [9] S. Udayakumar, M. Lee, H. Shim, S. Park, D.W. Park, *Catal. Commun.* 10 (2009) 659–664.
- [10] L. Han, H.J. Choi, S.J. Choi, B. Liu, D.W. Park, *Green Chem.* 13 (2011) 1023–1028.
- [11] K. Motokura, S. Itagaki, Y. Iwasawa, A. Miyaji, T. Baba, *Green Chem.* 11 (2009) 1876–1880.
- [12] Y. Xie, Z. Zhang, T. Jiang, J. He, B. Han, T. Wu, K. Ding, *Angew. Chem. Int. Ed.* 46 (2007) 7255–7258.
- [13] C. Aprile, F. Giacalone, P. Agrigento, L.F. Liotta, J.A. Martens, P.P. Pescarmona, M. Gruttaduria, *ChemSusChem* 4 (2011) 1830–1837.
- [14] C. Kohrt, T. Werner, *ChemSusChem* 8 (2015) 2031–2034.
- [15] C. Qi, J. Ye, W. Zheng, H. Jiang, *Adv. Synth. Catal.* 352 (2010) 1925–1933.
- [16] J. Sun, J. Wang, W. Cheng, J. Zhang, X. Li, S. Zhang, Y. She, *Green Chem.* 14 (2012) 654–660.
- [17] K.R. Roshan, G. Mathai, J. Kim, J. Tharun, G.A. Park, D.W. Park, *Green Chem.* 14 (2012) 2933–2940.
- [18] A.C. Kathalikkattil, J. Tharun, R. Roshan, H.G. Soek, D.W. Park, *Appl. Catal. A* 447–448 (2012) 107–114.
- [19] J. Tharun, Y. Hwang, R. Roshan, S. Ahn, A.C. Kathalikkattil, D.W. Park, *Catal. Sci. Technol.* 2 (2012) 1674–1680.

- [20] K.R. Roshan, J. Tharun, A.C. Kathalikkattil, D.W. Kim, B. Kim, D.W. Park, *Appl. Catal. A* 467 (2013) 17–25.
- [21] J. Melendez, M. North, R. Pasquale, *Eur. J. Inorg. Chem.* (2007) 3323–3326.
- [22] M. North, R. Pasquale, *Angew. Chem. Int. Ed.* 48 (2009) 2946–2948.
- [23] W. Clegg, W.R. Harrington, M. North, R. Pasquale, *Chem. Eur. J.* 16 (2010) 6828–6843.
- [24] A. Decortes, M. Martinez Belmonte, J. Benet-Buchholz, A.W. Kleij, *Chem. Commun.* 46 (2010) 4580–4582.
- [25] A. Decortes, A.W. Kleij, *ChemCatChem* 3 (2011) 831–834.
- [26] G. Salassa, M.J.J. Coenen, S.J. Wezenberg, B.L.M. Hendriksen, S. Speller, J.A.A.W. Elemans, A.W. Kleij, *J. Am. Chem. Soc.* 134 (2012) 7186–7192.
- [27] C.J. Whiteoak, N. Kielland, V. Laserna, E.C. Escudero-Adan, E. Martin, A.W. Kleij, *J. Am. Chem. Soc.* 135 (2013) 1228–1231.
- [28] J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang, C.Y. Su, *Chem. Soc. Rev.* 43 (2014) 6011–6061.
- [29] D. Farrusseng, S. Aguado, C. Pinel, *Angew. Chem. Int. Ed.* 48 (2009) 7502–7513.
- [30] J.Y. Lee, O.K. Farha, J. Roberts, K.A. Scheidt, S.T. Nguyen, J.T. Hupp, *Chem. Soc. Rev.* 38 (2009) 1450–1459.
- [31] A. Dhakshinamoorthy, A.M. Asiric, H. Garcia, *Chem. Soc. Rev.* 44 (2015) 1922–1947.
- [32] J. Gascon, A. Corma, F. Kapteijn, F.X. Llabres i Xamena, *ACS Catal.* 2 (2014) 361–378.
- [33] A.H. Chughtai, N. Ahmad, H.A. Younus, A. Laypkovc, F. Verpoort, *Chem. Soc. Rev.* (2015), <http://dx.doi.org/10.1039/C4CS00395K>.
- [34] M. Tu, R.J. Davis, *J. Catal.* 199 (2001) 85–91.
- [35] E.J. Doskocil, *Microporous Mesoporous Mater.* 76 (2004) 177–183.
- [36] E.J. Doskocil, *J. Phys. Chem. B* 109 (2005) 2315–2320.
- [37] H.Y. Ju, J.Y. Ahn, M.D. Manju, K.H. Kim, D.W. Park, *Korean J. Chem. Eng.* 25 (2008) 471–473.
- [38] J. Sun, S. Zhang, W. Cheng, J. Ren, *Tetrahedron Lett.* 49 (2008) 3588–3591.
- [39] H. Kawanami, A. Sasaki, K. Matsui, Y. Ikushima, *Chem. Commun.* 7 (2003) 896–897.
- [40] E.H. Lee, J.Y. Ahn, M.M. Dharman, D.W. Park, S.W. Park, I. Kim, *Catal. Today* 131 (2008) 130–134.
- [41] J. Sun, S. Ichiro, S. Fujita, M. Arai, *J. Organomet. Chem.* 690 (2005) 3490–3497.
- [42] J. Peng, Y. Deng, *New J. Chem.* 25 (2001) 639–641.
- [43] H. Kawanami, Y. Ikushima, *Chem. Commun.* 21 (2000) 2089–2090.
- [44] A. Barbarini, R. Maggi, A. Mazzacani, G. Mori, G. Sartori, R. Sartorio, *Tetrahedron Lett.* 44 (2003) 2931–2934.
- [45] J.W. Huang, M. Shi, *J. Org. Chem.* 68 (2003) 6705–6709.
- [46] H. Deng, C.J. Doonan, H. Furukawa, R.B. Ferreira, J. Towne, C.B. Knobler, B. Wang, O.M. Yaghi, *Science* 327 (2010) 846–850.
- [47] Y.J. Kim, D.W. Park, *J. Nanosci. Nanotechnol.* 13 (2013) 2307–2312.
- [48] M. Zhu, D. Srinivas, S. Bhogeswararao, P. Ratnasamy, M.A. Carreon, *Catal. Commun.* 32 (2013) 36–40.
- [49] O.V. Zalomaeva, A.M. Chibiryakov, K.A. Kovalenko, O.A. Kholdeeva, B.S. Balzhinimaev, V.P. Fedin, *J. Catal.* 298 (2013) 179–185.
- [50] A.C. Kathalikkattil, D.W. Park, *J. Nanosci. Nanotechnol.* 13 (2013) 2230–2235.
- [51] D.A. Yang, H.Y. Cho, J. Kim, S.T. Yang, W.S. Ahn, *Energy Environ. Sci.* 5 (2012) 6465–6473.
- [52] J. Kim, S.N. Kim, H.G. Jang, G. Seo, W.S. Ahn, *Appl. Catal. A* 453 (2013) 175–180.
- [53] H.Y. Cho, D.A. Yang, J. Kim, S.Y. Jeong, W.S. Ahn, *Catal. Today* 185 (2012) 35–40.
- [54] A.C. Kathalikkattil, D.W. Kim, J. Tharun, H.G. Soek, R. Roshan, D.W. Park, *Green Chem.* 16 (2014) 1607–1616.
- [55] A.C. Kathalikkattil, R. Roshan, J. Tharun, H.G. Soek, H.S. Ryu, D.W. Park, *ChemCatChem* 6 (2014) 284–292.
- [56] C.M. Miralda, E.E. Macias, M. Zhu, P. Ratnasamy, M.A. Carreon, *ACS Catal.* 2 (2012) 180–183.
- [57] T. Jose, Y. Hwang, D.W. Kim, M.I. Kim, D.W. Park, *Catal. Today* 245 (2015) 61–67.
- [58] M. Zhu, D. Srinivas, S. Bhogeswararao, P. Ratnasamy, M.A. Carreon, *Catal. Commun.* 32 (2013) 36–40.
- [59] L. Yang, L. Yu, G. Diao, M. Sun, G. Cheng, S. Chen, *J. Mol. Catal. A* 392 (2014) 278–283.
- [60] W. Morris, C.J. Doonan, H. Furukawa, R. Banerjee, O.M. Yaghi, *J. Am. Chem. Soc.* 130 (2008) 12626–12627.
- [61] R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O'Keeffe, O.M. Yaghi, *Science* 319 (2008) 939–943.
- [62] M. Aresta, A. Dibenedetto, A. Angelini, *Chem. Rev.* 114 (2014) 1709–1742.
- [63] J. Qian, F. Sun, L. Qin, *Mater. Lett.* 82 (2012) 220–223.
- [64] A. Schejin, A. Aboulaich, L. Balan, V. Falk, J. Lalevée, G. Medjahdi, L. Aranda, K. Mozeta, R. Schneider, *Catal. Sci. Technol.* 5 (2015) 1829–1839.
- [65] H. Yang, X.W. He, F. Wang, Y. Kang, J. Zhang, *J. Mater. Chem.* 22 (2012) 21849–21851.
- [66] Q. Shi, Z. Chen, Z. Song, J. Li, J. Dong, *Angew. Chem. Int. Ed.* 50 (2011) 672–675.
- [67] E.X. Chen, H.R. Fu, R. Lin, Y.X. Tan, J. Zhang, *ACS Appl. Mater. Interfaces* 6 (2014) 22871–22875.
- [68] E.X. Chen, H. Yang, J. Zhang, *Inorg. Chem.* 53 (2014) 5411–5413.
- [69] H. Yang, X.W. He, F. Wang, Y. Kang, J. Zhang, *J. Mater. Chem.* 22 (2012) 21849–21851.
- [70] L. Yang, L. Yu, M. Sun, C. Gao, *Catal. Commun.* 54 (2014) 86–90.
- [71] A. Corma, *Nat. Nanotech.* 9 (2014) 412.
- [72] R. Richards, *Surface and Nanomolecular Catalysis*, Taylor and Francis, 2006.
- [73] C. Chizallet, S. Lazare, D. Bazer-Bachi, F. Bonnier, V. Lecocq, E. Soyer, A.A. Quoineaud, N. Bats, *J. Am. Chem. Soc.* 132 (2010) 12365–12377.
- [74] B. Chen, Z. Yang, Y. Zhu, Y. Xia, *J. Mater. Chem. A* 2 (2014) 16811–16831.
- [75] J.Y. Lee, O.K. Farha, J. Roberts, K.A. Scheidt, S.B.T. Nguyen, J.T. Hupp, *Chem. Soc. Rev.* 38 (2009) 1450–1459.
- [76] K.R. Roshan, B.M. Kim, A.C. Kathalikkattil, J. Tharun, Y.S. Won, D.W. Park, *Chem. Commun.* 50 (2014) 13664–13667.
- [77] J. Tharun, G. Mathai, A.C. Kathalikkattil, R. Roshan, Y.S. Won, S.J. Cho, J.S. Chang, D.W. Park, *ChemPlusChem* 80 (2015) 715–7215.